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*Published in:*  
Journal of Molecular Catalysis

*DOI:*  
[10.1016/0304-5102\(81\)85034-1](https://doi.org/10.1016/0304-5102(81)85034-1)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1981

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

TEUBEN, JH., DEBOER, EJM., KLAZINGA, AH., KLEI, E., & Boer, E. J. M. D. (1981). CO ACTIVATION BY DICYCLOPENTADIENYL DERIVATIVES OF TITANIUM, NIOBIUM AND TANTALUM. *Journal of Molecular Catalysis*, 13(1), 107-114. [https://doi.org/10.1016/0304-5102\(81\)85034-1](https://doi.org/10.1016/0304-5102(81)85034-1)

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## CO ACTIVATION BY DICYCLOPENTADIENYL DERIVATIVES OF TITANIUM, NIOBIUM AND TANTALUM

J. H. TEUBEN, E. J. M. DE BOER<sup>†</sup>, A. H. KLAZINGA<sup>†</sup> and E. KLEI

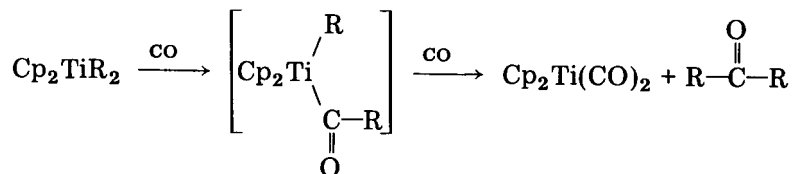
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### Summary

Exploratory studies on reactions of CO (room temperature, 1 atmosphere) with  $\text{Cp}_2\text{TiR}$  ( $\text{R}$  = aryl, alkyl, allyl, vinyl) and  $\text{Cp}_2\text{MR}$  ( $\text{M}$  = Nb, Ta;  $\text{R}$  = alkyl) are reported. The titanium compounds show formation of CO complexes  $\text{Cp}_2\text{Ti}(\text{CO})\text{R}$  for  $\text{R}$  = Cl,  $\text{C}_6\text{F}_5$ , and of  $\eta^2$ -acyl complexes  $\text{Cp}_2\text{TiCOR}$  for  $\text{R}$  =  $\text{C}_6\text{H}_5$ ,  $o\text{-CH}_3\text{C}_6\text{H}_4$ , and  $\text{C}(\text{CH}_3)=\text{C}(\text{H})\text{CH}_3$ . For  $\text{R}$  =  $\text{C}_6\text{H}_5$ ,  $\text{CH}_3$ ,  $\text{CH}_2\text{C}(\text{CH}_3)_3$  and  $\eta^3\text{-C}_3\text{H}_5$  more complicated reactions take place and complete identification of the products was not possible. The formation of ketones,  $\text{RCOR}$ , and diketones,  $\text{RCOCOR}$ , show the formation of new C-C bonds in these systems, possibly through the radical character induced on the ligands by back donation of the unpaired electron of titanium. Reduction of the acyl function and of ketones to the corresponding alcohols was observed. The niobium and tantalum compounds  $\text{Cp}_2\text{MR}$  ( $\text{R}$  =  $n\text{-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$ ,  $n\text{-C}_5\text{H}_{11}$ ) give stable complexes  $\text{Cp}_2\text{M}(\text{CO})\text{R}$  and further reaction of these with CO was not observed.

### Introduction

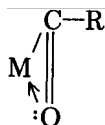
Carbon monoxide activation by early transition metal compounds has been shown to be a very promising field in CO chemistry. The first reports [1 - 3] on CO reacting with  $\text{Cp}_2\text{TiR}_2^*$  and  $\text{Cp}_2\text{Ti}(\text{R})\text{Cl}$  ( $\text{R}$  =  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ) showed, in addition to a facile insertion of the CO molecule into the Ti-C bond and reductive elimination of a ketone:



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\* $\text{Cp}$  =  $\eta^5\text{-C}_5\text{H}_5$ ,  $\text{Cp}^*$  =  $\eta^5\text{-C}_5\text{Me}_5$ .

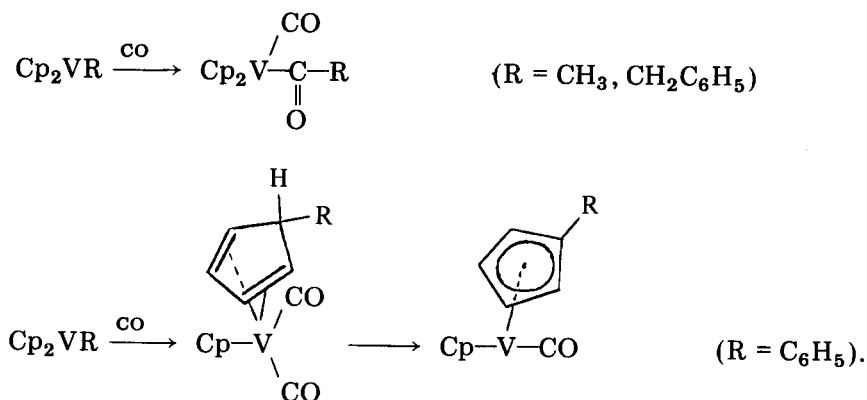
an interesting new *dihapto* bonding mode of the acyl group, *viz.*,



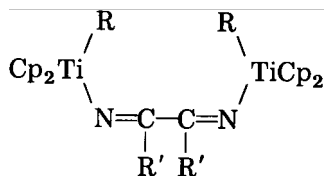
This type of bonding has been found to be quite common for early transition metals and underlines the high oxygen affinity of these metals [4, 5].

Quite recently elegant studies by Bercaw on the reaction of  $\text{Cp}_2^*\text{ZrH}_2$  with  $\text{Cp}_2^*\text{Zr}(\text{CO})_2$  and other metal carbonyls provided a clear insight into the mechanism of the reduction of CO to  $\text{CH}_3\text{OH}$  and the formation of the  $\text{M}-\text{O}-\text{CH}=\text{CH}-\text{O}-\text{M}$  complexes *via*  $\text{M}-\text{O}-\dot{\text{C}}-\text{H}$  intermediates [6].

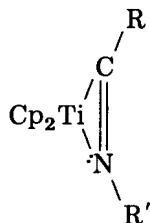
Group VB dicyclopentadienyl compounds seem to react differently. Floriani reported the reaction of  $\text{Cp}_2\text{VR}$  with CO [5]. Depending on R, CO can be inserted to give  $\text{Cp}_2\text{V}(\text{CO})\text{COR}$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$ ) or R is transferred to the cyclopentadienyl ring ( $\text{R} = \text{C}_6\text{H}_5$ ):



The aforementioned starting compounds and products are all even (16 or 18) electron systems. We decided to study the reactions of odd (15) electron systems,  $\text{Cp}_2\text{TiR}$ . The unpaired electron can here be transferred by  $\pi$ -back-donation on to the ligand, giving radical character to certain parts of the molecule and possibly, in consequence, interesting reactions. We found such reactions when  $\text{Cp}_2\text{TiR}$  ( $\text{R} = \text{aryl}$ ) was reacted with cyanides  $\text{R}'\text{CN}$  and isocyanides  $\text{R}'\text{NC}$ . With cyanides, coupling of the ligands *via* the cyanide C-atom was observed with the formation of [7]:



Isocyanides insert into the Ti-C bond giving  $\eta^2$ -iminoacyl complexes [8]



We have extended our studies to the reaction of  $\text{Cp}_2\text{TiR}$  ( $\text{R}$  = aryl, alkyl, allyl, vinyl) with CO. We also investigated the reactions of  $\text{Cp}_2\text{MR}$  ( $\text{M}$  = Nb, Ta;  $\text{R}$  = alkyl) with CO to compare the results with those of  $\text{Cp}_2\text{TiR}$  and  $\text{Cp}_2\text{VR}$ . In the 'hypothetical' compounds  $\text{Cp}_2\text{MR}$  ( $\text{M}$  = Nb, Ta), the size of the metals is expected to be about the same as Ti; V is smaller. Steric aspects will be very similar for the compounds  $\text{Cp}_2\text{MR}$  ( $\text{M}$  = Ti, Nb, Ta) but the electronic aspects are quite different. The Nb and Ta complexes have two electrons available for back donation whereas the titanium compounds have one. By studying the complexes we believe we have a distinct possibility of finding an effect which depends on the number of electrons available for back-donation.

In this communication we report the results of some exploratory studies. Parts of the study have been published elsewhere [9, 10].

## Experimental

Data on experimental conditions, equipment, and analytical procedures can be found elsewhere [9, 10].

The compounds were prepared following published procedures:  $\text{Cp}_2^*\text{TiCl}$  [10],  $\text{Cp}_2\text{TiR}$  ( $\text{R}$  =  $\text{C}_6\text{F}_5$ ,  $\text{C}_6\text{H}_5$ ,  $o\text{-CH}_3\text{C}_6\text{H}_4$ ) [17],  $\text{Cp}_2\text{TiCH}_3$  [18],  $\text{Cp}_2\text{TiCH}_2\text{C}(\text{CH}_3)_3$  [19],  $\text{Cp}_2\text{Ti}(\eta^3\text{-C}_3\text{H}_5)$  [20],  $\text{Cp}_2\text{MR}$  ( $\text{M}$  = Nb, Ta) [9].

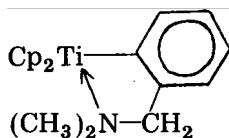
$\text{Cp}_2\text{TiC}(\text{CH}_3)=\text{C}(\text{H})\text{CH}_3$  was prepared from  $(\text{Cp}_2\text{TiCl})_2$  and  $\text{LiC}(\text{CH}_3)=\text{C}(\text{H})\text{CH}_3$ . It was isolated and fully characterized [21].

## Results and discussion

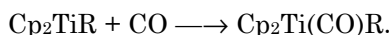
### *Titanium compounds $\text{Cp}_2\text{TiR}$*

Almost all 15-electron compounds,  $\text{Cp}_2\text{TiR}$ , react easily with CO (25 °C, 1 atm) both in solution and in the solid state. The products mainly depend on the nature of R; other variables such as solvent or temperature seem to be of secondary importance.

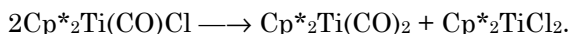
No reaction takes place with complexes where the vacant site on the metal is inaccessible. This can be for steric reasons (*e.g.*,  $\text{Cp}_2\text{Ti-2,6-(CH}_3)_2\text{C}_6\text{H}_3$  [11]) or due to coordination with heteroatom donor ligands (*e.g.*, in dimeric  $(\text{Cp}_2\text{TiCl})_2$  [12], or in the internally coordinated compound below [13].



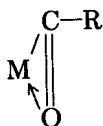
For strong electronegative R groups, (R = Cl\*, C<sub>6</sub>F<sub>5</sub>), the reaction proceeds according to:



For R = C<sub>6</sub>F<sub>5</sub> the adduct could be isolated and characterized completely; Cp\*<sub>2</sub>Ti(CO)Cl is thermally unstable and disproportionates:



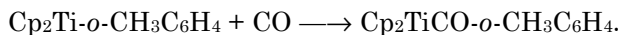
The adducts are terminal CO complexes showing  $\nu(\text{CO})$  at 2060 (R = C<sub>6</sub>F<sub>5</sub>) and 2020 cm<sup>-1</sup> (R = Cl) [10]. They are comparable with the vanadium complex Cp<sub>2</sub>V(CO)Cl ( $\nu(\text{CO})$  1950 cm<sup>-1</sup>) [5] taking into account that Cp<sub>2</sub>VCl (16 electron system) has two, and the titanium compounds have only one electron available for  $\pi$ -bonding with the CO ligand. The formation of Cp\*<sub>2</sub>Ti(CO)<sub>2</sub> from Cp\*<sub>2</sub>Ti(CO)Cl resembles in a way the formation of Cp<sub>2</sub>Ti(CO)<sub>2</sub> from Cp<sub>2</sub>TiR<sub>2</sub> (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) and CO. In the latter case it is thought to result from carbonylation of titanocene formed by the reductive elimination of the ketone R–CO–R from the acyl alkyl compound Cp<sub>2</sub>Ti(COR)R [2]. In the case of Cp\*<sub>2</sub>Ti(CO)Cl, at least an intermolecular reaction is needed to explain the products. The chemical reactivity of the CO molecule in these adducts is rather low. Despite the preference of early transition metals for insertion of CO into an M–C bond to give an  $\eta^2$ -acyl,



this is not observed here. Instead the CO ligand is easily lost with formation of the original Cp<sub>2</sub>TiR (R = C<sub>6</sub>F<sub>5</sub>) by warming a solution of the adduct under reduced pressure.

Less electronegative R groups (aryl, alkyl, allyl, vinyl) at once give insertion of CO into the Ti–R bond accompanied by side- and following reactions resulting in very complex mixtures. It is very probable that the insertion step is preceded by adduct formation, a process that has been observed in the closely related systems of Cp<sub>2</sub>TiR with cyanides R'CN and isocyanides R'NC [7, 8].

So far the only acyl compound sufficiently stable to isolate and study is Cp<sub>2</sub>TiCO-*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>:

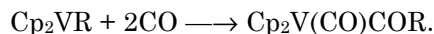


Its stability is probably due to the steric interaction of the *ortho* methyl group on the phenyl ring which shields the acyl carbon atom from further interaction with other titanium compounds. The acyl group is  $\eta^2$ -bonded to the metal as can be concluded from the very low, characteristic  $\nu(\text{C}=\text{O})$  at 1470 cm<sup>-1</sup> [3].

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\*In this case the permethyl complex Cp\*<sub>2</sub>TiCl (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) was studied because it is monomeric in solution.

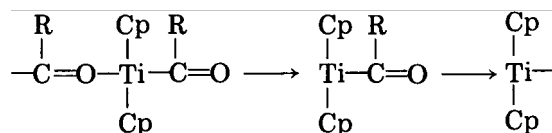
Acyl formation was also found for  $\text{Cp}_2\text{VR}$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$ ) [5]. Here the insertion of CO into a V–C bond is accompanied by complexation of an extra CO molecule:



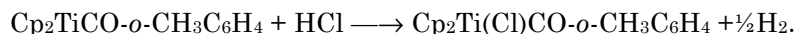
For  $\text{Cp}_2\text{Ti}-o\text{-CH}_3\text{C}_6\text{H}_4$  no further uptake of CO was observed. The availability of one electron may be insufficient to give the back donation needed to bind an additional CO molecule, the bonding of the  $\eta^2$ -acyl may be too strong, but steric reasons may also be responsible for this difference between vanadium and titanium compounds  $\text{Cp}_2\text{VR}$ .

Oxidation of  $\text{Cp}_2\text{TiCo}-o\text{-CH}_3\text{C}_6\text{H}_4$  with the disulfide  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$  or iodine gives the diamagnetic, tetravalent compounds  $\text{Cp}_2\text{Ti}(\text{X})\text{CO}-o\text{-CH}_3\text{C}_6\text{H}_4$  ( $\text{X} = \text{I}, \text{C}_6\text{H}_5\text{S}$ ). The observed  $\nu(\text{C}=\text{O})$  ( $1570 - 1580 \text{ cm}^{-1}$ ) is now in a position comparable with the closely related  $\text{Cp}_2\text{Ti}(\text{I})\text{COCH}_3$  ( $\nu(\text{C}=\text{O})$   $1610 \text{ cm}^{-1}$ ) [3].

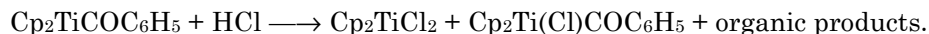
The reaction of CO with  $\text{Cp}_2\text{TiC}_6\text{H}_5$  is similar but more complicated, and the products could not be identified in detail. The uptake of CO (in the case of  $\text{Cp}_2\text{Ti}-o\text{-CH}_3\text{C}_6\text{H}_4$  exactly 1 CO/Ti) varies for different runs between 1.3 and 1.8 CO/Ti. The i.r. spectrum shows an absorption at  $1500 \text{ cm}^{-1}$  indicative of  $\eta^2$ -acyl, but the low solubility suggests oligomeric or polymeric structures with bridging acyls:



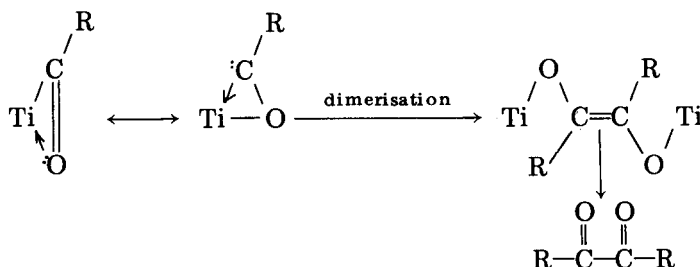
The reaction of  $\text{Cp}_2\text{TiCOR}$  with HCl/ether was studied. For  $\text{R} = o\text{-CH}_3\text{C}_6\text{H}_4$  the acyl was oxidized quantitatively:



For  $\text{R} = \text{C}_6\text{H}_5$  a complex mixture resulted:

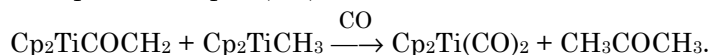


The Ti-balance for the products does not add up to 100% and unidentified organotitanium compounds are still present. The organic part of the reaction product is very complicated. The presence of  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{CO-COC}_6\text{H}_5$  was demonstrated. The fact that coupling products such as biphenyl and  $\text{C}_6\text{H}_5\text{CO-COC}_6\text{H}_5$  are present indicate radical character. It is not clear whether this coupling takes place in the reaction with CO or in the HCl reaction. The presence of  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Cp}_2\text{Ti}(\text{Cl})\text{COC}_6\text{H}_5$  show - at least in part - the retention of the  $\text{Cp}_2\text{Ti}$  structure during the carbonylation and work up. This is in contrast to the carbonylation of  $\text{Cp}_2\text{VC}_6\text{H}_5$ , where the aryl group is transferred to the cyclopentadienyl ring. A very interesting point is the presence of the diketone  $\text{C}_6\text{H}_5\text{CO-COC}_6\text{H}_5$ , because it suggests a strong relation between the CO reactions in these systems and the Bercaw systems  $\text{Cp}^*\text{ZrH}_2/\text{CO}$ ; the mechanisms of the reactions may show close similarity [6].



However, other mechanisms are conceivable.

Carbonylation of  $\text{Cp}_2\text{TiCH}_3$  results in a complicated mixture of products. The main difference from the aryl compounds is the formation of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (33%) and acetone, isopropyl alcohol and ethanol in minor quantities. Probably, reaction of  $\text{Cp}_2\text{TiCOCH}_3$  with unreacted  $\text{Cp}_2\text{TiCH}_3$  under CO produces  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and acetone:

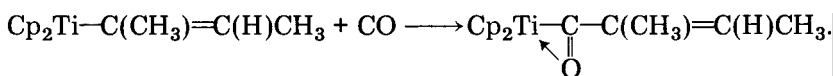


It resembles to some degree the formation of acetone from  $\text{Cp}_2\text{Ti}(\text{COCH}_3)\text{Cl}$  with  $\text{CH}_3\text{MgCl}$  under CO [2]; in our case, free  $\text{Cp}_2\text{TiCH}_3$  would play the role of the Grignard reagent.

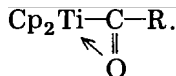
The presence of ethanol and 2-propanol indicates a reduction of a carbonyl function during the reaction. Hydrogen for this process may be supplied by various sources, *e.g.*, cyclopentadienyl ligands, methyl groups or solvent molecules [14].

Attempts to control the carbonylation reaction and isolate the acyl  $\text{Cp}_2\text{TiCOR}$  were undertaken for  $\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_3$ , but were unsuccessful. The results are basically the same as those obtained for  $\text{Cp}_2\text{TiCH}_3$ .

Carbonylation of  $\text{Cp}_2\text{Ti}(\eta^3\text{-C}_3\text{H}_5)$  ( $= \text{Cp}_2\text{Ti-}\pi\text{-allyl}$ ) is a rather simple reaction,  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $(\text{C}_3\text{H}_5)_2\text{CO}$  being the main products. It is also observed for  $\text{Cp}_2\text{TiR}$  ( $\text{R} = \text{alkyl}$ ) but there it is a minor reaction. The  $\eta^3$ -coordination of the allyl group apparently limits the number of possible reactions essentially to one. The vinyl derivative  $\text{Cp}_2\text{Ti-C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{H}$  also gives a clear result but different from that of the allyl compound:



The acyl can be isolated in good yield and characterized ( $\nu(\text{CO})$  1482  $\text{cm}^{-1}$ ) as a normal paramagnetic  $\eta^2$ -acyl compound,

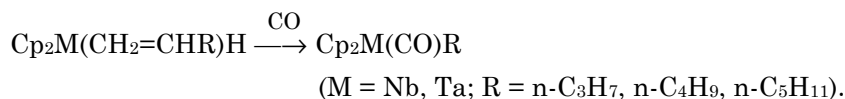


It can be oxidized by  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$  to the diamagnetic tetravalent  $\text{Cp}_2\text{Ti}(\text{SC}_6\text{H}_5)(\text{CO})\text{-C}(\text{CH}_3)=\text{C}(\text{H})\text{CH}_3$  ( $\nu(\text{CO})$  1564  $\text{cm}^{-1}$ ) and shows close analogy with  $\text{R} = o\text{-tolyl}$ .

The reason for the different course of the carbonylation reactions for  $\eta^3$ -allyl and vinyl compounds  $\text{Cp}_2\text{TiR}$  is not clear.

### Niobium and tantalum compounds $\text{Cp}_2\text{MR}$

The niobium and tantalum compounds  $\text{Cp}_2\text{MR}$  (R = alkyl, aryl) are not known. Their complexes  $\text{Cp}_2\text{MRL}$  can, however, be easily formed by reaction of *endo*-olefin-hydride complexes  $\text{Cp}_2\text{M}(\text{CH}_2=\text{CHR})\text{H}$  with donor-acceptor ligands, L, such as CO or isocyanides [9]:



The  $\nu(\text{CO})$  absorptions are found at 1880 - 1925 cm<sup>-1</sup>, indicating considerable back donation from the metal into the  $\pi^*$ -orbitals of the CO molecule. In consequence, the CO molecule is firmly bound to the metal and the ligand shows little reactivity. Formation of the acyl complexes  $\text{Cp}_2\text{MCOR}$ , commonly found for titanium and vanadium [5, 10], was not observed. By contrast, the CO complexes  $\text{Cp}_2\text{M}(\text{CO})\text{R}$  are thermally rather robust. Decomposition with loss of CO is observed for M = Nb from about 130 °C; for M = Ta, decomposition sets in at about 150 °C. In this respect they behave like  $\text{Cp}_2\text{Ti}(\text{CO})\text{C}_6\text{F}_5$ . The low reactivity of the Nb and Ta alkyl carbonyl complexes with respect to V is surprising, since on going from 3d to 4d or 5d metal compounds the latter are often more reactive than their 3d analogues (*cf.* CO reactions of  $\text{Cp}_2\text{MR}_2$ , M = Ti, Zr, Hf [2, 3, 15]). On the other hand our results seem to fit in with observations by other workers; *e.g.*,  $\text{Cp}_2\text{Nb}(\text{CO})\text{COC}_2\text{H}_5$  could be produced from  $\text{Cp}_2\text{Nb}(\text{C}_2\text{H}_4)\text{C}_2\text{H}_5$  by high temperature and CO pressure, and  $\text{Cp}_2\text{Nb}(\text{CO})\text{CH}_3$  does not react with CO under reflux in benzene in a CO atmosphere [16].

### Acknowledgements

The authors thank Prof. Dr H. J. de Liefde Meijer and Prof. Dr F. Jellinek for their stimulating interest. Mrs A. Jonkman-Beuker is thanked for her able experimental assistance. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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